



The influence of kinetics, mass transfer and catalyst deactivation on the growth rate of multiwalled carbon nanotubes from ethene on a cobalt-based catalyst



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HIGHLIGHTS

- Reaction kinetics of multiwalled CNT growth was determined by systematic variation of temperature and ethene concentration.
- Data were evaluated with a dynamic reactor model taking into account film and pore diffusion as well as agglomerate growth.
- CNT growth kinetics is first order in ethene concentration at an activation energy of 107 kJ/mol.
- Deactivation kinetics is second order in consumed amount of ethene.

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ABSTRACT

CNT growth experiments on a cobalt-based catalyst were conducted in a tubular fixed bed reactor at different temperatures and ethene concentrations. The measured kinetic data were analyzed with an isothermal, dynamic reactor model taking into account pore and film diffusion as well as the size of CNT agglomerates as a function of time. Based on previously published results it was found that the CNT agglomerates are enlarged by an average factor of 6.5 compared to the original diameter of the catalyst particle. Under these conditions, the development of the agglomerate diameter with time can be described with a single parameter which is independent of the reaction conditions. The rate of the CNT growth was determined to be first order in the ethene concentration with an activation energy of 107 kJ/mol. The catalyst deactivation by cumulative encapsulation of active sites was found to be second order with respect to the consumed amount of ethene with a rate constant independent of the temperature. Nevertheless, deactivation takes place faster at higher temperatures and/or ethene concentrations, since the deactivation process is directly coupled to the rate of CNT synthesis.

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1. Introduction

Multiwalled carbon nanotubes have many extraordinary properties such as their unique geometry, high electrical and thermal conductivity as well as high mechanical strength [1,2]. Therefore the synthesis of CNTs has been intensively studied and the growing number of potential applications results in an increasing demand for inexpensive CNTs [3,4]. Catalytic chemical vapor deposition (CCVD) of hydrocarbons over transition metal catalysts (e.g. Fe, Co and Ni) is the most promising synthesis route towards large-scale CNT production [5,6]. During the last years the first pilot plant CCVD reactors have been built and are now capable of producing several hundred tons of CNTs per year [7,8]. The state of

the art in CNT development and manufacture has recently been reviewed by Mleczko and Lolli [9].

For the design of large-scale plants and further process optimization, detailed knowledge of the CNT reaction kinetics is essential. Furthermore, kinetic models can be used to identify reaction pathways and to describe the formation of byproducts [10]. The growth kinetics of vertically aligned CNTs has been described frequently in literature, since their well-defined morphology allows an easy measurement of CNT length and amount of converted carbon precursor [11–19]. A simple kinetic model describing the length of aligned CNTs as a function of time has been presented by Hata et al. [20,21]. In a previous publication we have shown that the mass accumulation of agglomerated CNTs can also be predicted with this approach [22].

Only few studies have dealt with monitoring the growth kinetics of agglomerated CNTs by on-line analysis of the effluent gas composition. Pirard et al. measured the concentration of released

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Nomenclature

B_0	permeability (m^2)	x	mole fraction, dimensionless
Bo	Bodenstein number, dimensionless	Y	yield ($\text{kg}_{\text{CNT}}/\text{kg}_{\text{Cat}}$)
c	concentration (mol/m^3)	z	coordinate (m)
D	dispersion coefficient (m^2/s)		
D_{ij}^e	effective bulk diffusivity in porous medium (m^2/s)	Greek symbols	
$D_{i,K}^e$	effective Knudsen diffusivity in porous medium (m^2/s)	θ	encapsulation ratio, dimensionless
d	diameter (m)	η	dynamic viscosity (Pa s)
E_A	activation energy (kJ/mol)	η_{Cat}	catalyst effectiveness, dimensionless
k	constant in Eq. (8), dimensionless	ρ	bulk density, $\text{kg}_{\text{Cat}}/\text{m}^3_{\text{R}}$
k_0	frequency factor for CNT synthesis ($\text{m}^3/(\text{kg s})$)	ν	stoichiometric coefficient, dimensionless
k_{Des}	reaction rate constant for deactivation ($\text{kg}^2/(\text{mol}^2 \text{s}^2)$)	χ	growth ratio, dimensionless
L	reactor length (m)		
N	flux ($\text{mol}/(\text{m}^2 \text{s})$)	Subscripts	
n	reaction order, dimensionless	agg	CNT agglomerate
$n_i^{\text{converted}}$	amount of converted component i (mol)	Cat	catalyst
p	pressure (Pa)	i	component i
R	ideal gas constant, 8.3143 J/mol K	j	component j
r	reaction rate ($\text{mol}/\text{m}^3 \text{ s}$)	max	maximum
T	temperature (K)	R	reactor
t	time (s)	t	total
u	velocity (m/s)		
V	volume (m^3)		

hydrogen by using mass spectrometry, which allowed for indirect quantification of the converted carbon precursor [23,24]. Gomme et al. were able to analyze the complete product spectrum during CNT synthesis, also using mass spectrometry [25]. Phillippe et al. performed kinetic experiments in a fluidized bed reactor using gas chromatography by taking gas samples every 10 min [26].

In this work a series of fixed bed experiments on a reduced Co–Mn–Al–Mg mixed oxide catalyst [27] with ethene as precursor gas was performed. Both the ethene inlet concentration and the reaction temperature were varied. Based on the measured effluent gas composition as a function of time and using a fixed-bed reactor model, a kinetic equation describing both CNT growth and catalyst deactivation was developed. Based on previous measurements of the agglomerate size as a function of time over single catalyst particles [28], the influence of diffusion processes on the measured rate could also be quantitatively described.

2. Material and methods

The CNT growth experiments were performed in a fixed bed reactor consisting of a U-shaped quartz tube with a length of 534 mm and an inner diameter of 7 mm. Before the growth experiments, the flow cell detector was calibrated to the ethene concentration of the feed gas mixture that consisted of 57 sccm C_2H_4 (99.95%), 43 sccm H_2 (99.999%), and 50 sccm Ar (99.999%). The catalyst, which was thoroughly characterized in earlier studies [29,30], had a BET surface area in the range of 122–133 m^2/g and a narrow pore size distribution between 4 and 8 nm. About 5 mg of the calcined catalyst grains with a mean particle diameter of $302 \mu\text{m} \pm 52 \mu\text{m}$ were weighed and placed on a quartz wool plug inside the second branch of the U-shaped reactor. An additional quartz wool plug was placed 20 mm above the catalyst bed to avoid any discharge of particles or CNT agglomerates. The loaded reactor was weighed as a whole on an analytical balance. Prior to installation in the setup a quartz rod with a diameter of 6 mm was placed inside the first branch of the reactor in order to reduce its inner volume. The connected reactor was purged with pure Ar for 10 min to remove air and moisture. After purging the catalyst was reduced in a gas mixture of 75 sccm H_2 and 75 sccm Ar from

room temperature to 650 °C applying a heating rate of 10 K min^{-1} with 5 min additional hold time. The reactor was purged again with pure Ar for 10 min at 650 °C and closed by switching the reactor valve to the offline position. The desired flow of feed gas was introduced to the system and the baseline of ethene in the effluent gas was recorded by the detector with a sampling rate of 1.0 s^{-1} for 5 min. The CNT growth reaction was started by switching the reactor online. Further details of the evaluation of the measured data can be found in [22].

The growth experiment was stopped after 5 min by switching the gas flow from feed gas to pure Ar, while keeping the total flow rate of 150 sccm. After purging for 10 min the reactor was cooled in Ar to room temperature and disconnected from the setup. The quartz rod was removed and the reactor was weighed again as a whole. Photographs of the loaded quartz reactor before and after a growth experiment are shown in Fig. 1.

The growth reactions were performed at the following temperatures: 600, 625, 650, 675 and 700 °C. To ensure comparability the experiments were conducted using the same batch of catalyst. For

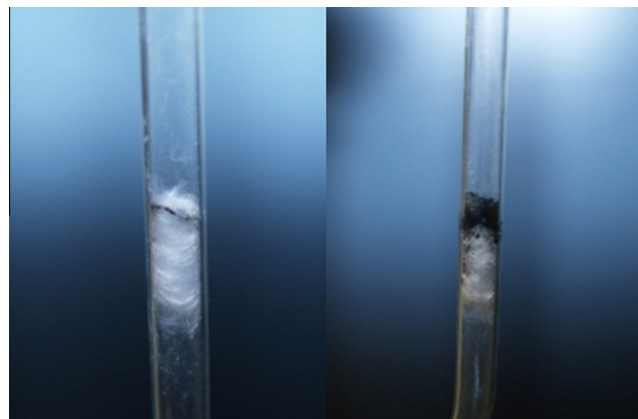


Fig. 1. Left: tube reactor with catalyst; right: CNTs after a growth experiment with a duration of 5 min.

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